Atmospheric Chemistry and Physics Discussions

Interactive Comment

Interactive comment on "Uptake study of ClONO$_2$ and BrONO$_2$ by water droplets" by G. Deiber et al.

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Uptake study of ClONO2 and BrONO2 by halide containing droplets

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Authors comments to Anonymous Referee #1

We thank the referee for his very detailed comments.

As our data are of potential interest for the halogen budget of the marine boundary layer and because these are the first experiments on the uptake and reaction of ClONO2 and BrONO2 with halide solutions, we prepared a revised version of our manuscript in which we took into accounts all comments made by referee #1.

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We hope that this revised will be accepted in ACP.

Below, is our point per point response to the comments made by referee #1. For this purpose, for each, we first list the criticism of the reviewer followed by our response.

Title: Why are halide solutions not mentioned in the title? Most experiments appear to have been conducted on halide solutions, not water droplets.

The title of the manuscript has been changed in order to reflect more precisely its content.

Abstract. The 1 % statistical errors given for a-ClONO2 are wrong (see later)

The reported errors have been modified. They correspond in fact to 2s + 20%. This typesetting error has been fixed.

Page 1313, Line 14 and equations (2) and (3) "all these compounds are then rapidly photolysed" This is rather ambiguous. In which phase are these species, aqueous- or gas-phase ? Do the authors include the nitrates in this statement or are they referring only to the di-halogens ? Are they photolysed in the aqueous-phase, or are they transferred to the gas-phase beforehand ? Clarify and expand the text.

The text has been modified to: "These di-halogens compounds are only poorly soluble and will first desorb into the gas phase before being rapidly photolysed to generate either Cl or Br atoms, therefore having potentially a strong impact on the oxidation capacity of the marine boundary layer. "

Page 1313, Line 22 (also 1314, Line 1) and Page 1322 Line 4 What exactly is solid NaCl and NaBr. Are these experiments on single crystal surfaces, or powder samples. What was the relative humidity. Describe the salt surfaces with which you compare your results more thoroughly.

In the introduction we now present more thoroughly the framework in which we made our experiments, which highlights the need for uptake studies of both ClONO2 and

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BrONO2. "ĔThe heterogeneous reactions of ClONO2 with solid NaCl and KBr have already been studied in a fast flow reactor (Timonen et al., 1994) and a Knudsen cell (Caloz et al, 1996 ; Aguzzi et Rossi, 1999 ; Gebel and Finlayson-Pitts, 2001) and the primary reaction products on NaCl were HOCl and Cl2 while BrCl was observed on KBr. The heterogeneous reactions of BrONO2 with solid alkali halides have also been investigated in a Teflon-coated Knudsen flow reactor at ambient temperature (Aguzzi and Rossi, 1999). For solid NaCl substrates, BrCl, Br2 and HCl were observed as products while for KBr both Br2 and HBr were detected. This illustrates the fact that the reaction mechanism may not be as simple as a direct reaction of the halide ion on BrONO2. All these experiments were conducted over different solid substrates corresponding to powders (Timonen et al., 1994 ; Caloz et al., 1996 ; Gebel et al., 2001), spray deposited films, grains of various sizes and also single crystals (Caloz et al., 1996 ; Aguzzi and Rossi, 1999). Most of these experiments were also performed at low pressure (e.g. needed to achieve molecular transport in the Knudsen cell regime) which means that the gas phase humidity was very low. Nevertheless, even at such low pressures a certain amount of water is adsorbed on the salt surface and can only be (partially) pumped off when heated above 100°C. Such treatment was used in the studies on solid substrates which were accordingly performed on "dry" solids. However in the marine boundary layer (MBL), the relative humidity is high, reaching often more than 90%. As the deliquescence and efflorescence points of NaCl are 75% and 43% respectively, a very large fraction of sea-salt aerosols is wet. As the relative humidity is controlled by the temperature gradient, only under specifically cold situations or during a rapid up-lifting of an air mass, the humidity might get low enough to dry locally the sea-salts. Therefore, one may argue that a significant fraction of sea-salt aerosols in the MBL is wet. However, the uptake kinetics of XONO2 on liquid salt solutions has not been reported yet. In this work, we report the first measurements of uptake coefficients, using the droplet train technique, for ClONO2 and BrONO2 on pure water droplets or on aqueous solutions containing NaCl or NaBr (in order to mimic sea-salt particles) over the temperatures range 273 - 285 K. Some reaction products have also

been identified, suggesting some reaction mechanisms. In the following sections, we present our experimental methodology whereas in the subsequent section, we present and discuss the results of the uptake rate measurements."

Page 1314, Line 5 [For BrONO2] "the reaction may not be as simple as the one depicted by reactions (2) and (3)." This is certainly true as reactions (2) and (3) do not contain any bromine nitrate at all ! The equivalent reactions for bromine nitrate should be added.

Adding these reactions in the introduction will not help in keeping the text concise enough. The reactions were therefore not added but the text slightly modified to avoid any misundertaings. This paragraph is now written as: "The heterogeneous reactions of BrONO2 with solid alkali halides have also been investigated in a Teflon-coated Knudsen flow reactor at ambient temperature (Aguzzi and Rossi, 1999). For solid NaCl substrates, BrCl, Br2 and HCl were observed as products while for KBr both Br2 and HBr were detected. This illustrates the fact that the reaction mechanism may not be as simple as a direct reaction of the halide ion on BrONO2."

Page 1314, Line 7 What does "eventually" mean here ? "inevitably" or "usually" or "maybe" ? "one may argue that a significant fraction of sea-salt aerosols are wet". Rather than giving such qualitative statements why not be quantitative and say what the typical RH is in the MBL, and compare this to the deliquescence point of sea-salt particles is.

The text was widely changed in the revised manuscript: "However in the marine boundary layer (MBL), the relative humidity is high, reaching often more than 90%. As the deliquescence and efflorescence points of NaCl are 75% and 43% respectively, a very large fraction of sea-salt aerosols is wet. As the relative humidity is controlled by the temperature gradient, only under specifically cold situations or during a rapid up-lifting of an air mass, the humidity might get low enough to dry locally the sea-salts. Therefore, one may argue that a significant fraction of sea-salt aerosols in the MBL is wet.

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However, the uptake kinetics of XONO2 on liquid salt solutions has not been reported yet."

Page 1316, Line 16-27. Only qualitative information about the detection systems is given. What were the detection limits. What concentrations were used ? What molecules were detected with which system ? In the experimental section, we try now to be more quantitative both describing in more details the purity of our gases and the analytical devices that has been used to monitor the gas phase concentrations of products and reactants: The gas stream coming out of the flowtube was mainly analysed using an ion trap mass spectrometer operated with an ionisation energy of 60 eV. The signal was averaged over a second in order to increase the signal to noise ratio. $ClONO_2$ was monitored at 51 amu (ClO^+), $BrONO_2$ at 95 and 97 amu (BrO^+), Cl_2, $BrCl$, Br_2, by their parent ions (70, 116 and 160 amu respectively). In addition, H_2O and an inert tracer SF_6 were monitored at 18 (H_2O^+) amu and 89 ($S+F_3$) amu during the experiments in order to see any potential perturbations in gas phase concentrations. All these masses were chosen in order to minimize potential cross contributions to the signal which might result in incorrect interpretations. We also used FTIR spectroscopy in order to complete the gas phase analysis (especially during the synthesis of the reactants). The system used consists of a Nicolet Protégé 460 spectrometer equipped with an IRA long path White-cell (light path in the range 2.2 - 22 m) with KBr windows. Infra-red spectra were taken in the range 4000 to 400 cm-1 and were co-added in order to increase the S/N ratio. This FTIR set-up was mainly used to monitor nitrogen oxides (NO_2, N_2O_5) that may be present as impurities (see synthesis of gas phase reactants below) whereas the mass spectrometer was used to monitor halogen containing compounds. Both analytical devices were operated in uncalibrated mode as only the relative decay of the gas phase reactants has to be known in order to derive uptake coefficients. However, the linear response of the detector was routinely verified. For halogen containing compounds the masses were unambiguous markers for the gas phase reactants and were associated with detection limits of the order of 1012 molecule cm-3. The gas phase concentrations were estimated to range from 1013 to

1015 molecule cm-3.

Page 1318, Line 3 Why cite Caloz 1997 here. Was this the first time ClONO2 was made by this reaction ?

We assume here that the page given by the referee is 1317 and not 1318. We cite this reference work because the experimental protocol on synthesis of ClONO2 was well detailed by Caloz.

P1318, equation (8) The terms (diff), (sat) and (rxn) are not defined. In the part of the equation in parentheses: Should the "root" symbol not include the "t" ?

The terms g(diff), g(sat) and g(rxn) have been defined. The error in the equation has been also corrected: "the terms denoted gdiff, gsat and grxn correspond to the incoming flux driven respectively by gas phase diffusion, saturation and diffusion in the liquid phase and existing chemical aqueous phase reactions."

Page 1319, Line 27-28 "The measured kinetic is not elementary kinetic" Perhaps "the measured rate of loss of ClONO2 is driven by several..... would be better.

This suggestion has been taken account.

Page 1320, equation (9) The reaction does not balance. Na should be H

It was corrected.

Page 1320, Line 14 "We did not observe any increase of the uptake coefficient when adding NaCl to the droplets, but we observed some Cl2 production." Once again, this needs to be quantitative: how much NaCl was added ? (presumably to an aqueous sample that was used to generate the droplets, and not to the droplets themselves): How much Cl2 was formed ?

Such information is far beyond the capacity of the droplet train technique. In fact, the only quantitative information we can deliver concern the uptake coefficient. We can however, from our experimental results, discuss in a qualitative way a few aspects of

the chemistry of both ClONO2 and BrONO2. We have tried in the revised manuscript to make a more distinct difference between both quantitative and qualitative aspects of our study.

Page 1320, Line 19 As the authors mention in the next line, this reaction involves H+ in the aqueous phase, i.e. HOCl + H+ + Cl- = Cl2 + H2O. i.e. the rate of Cl2 production depends both on H+ and Cl-. If the authors wish to claim that the HOCl itself is the source of H+, then the dependence of the Cl2 production rate will be very non-linear in HOCl or ClONO2. Was this observed ? Exactly how is this self-acidification mechanism proposed to operate? In what form is HOCl in aqueous solution at high pH (i.e. what is the pKa ?) Aqueousphase studies show that the yield of Cl2 must depend on pH. As this is an important parameter, why did the authors not make a systematic investigation of pH ? The authors might consider the other product of the ClONO2 hydrolysis, which is HNO3. Could this provide the acidity ? If so, what are the characteristic times for reaction versus diffusion out of the droplet for HOCl ? Some quantitative discussion is necessary here.! In the same context: "dissociation of HOCl at the surface may affect the surface pH because this region is very narrow". What region are the authors referring to ? Presumably the region close to the surface, in which the reaction takes place and which is defined by the diffuso-reactive length ? Could the authors please state what "very narrow" means in more quantitative terms. There are kinetic data describing the aqueous phase reaction of HOCl with Cl- that enable calculation of this length.

Reaction (11) and the text have been modified: "Rather, we suggest a two-step mechanism where ClONO2 is first hydrolyzed according to reaction (9) to produce HOCl which subsequently reacts with NaCl according to: HOCl + Cl- +H+ -> Cl2 + H2O (11) In this case, the uptake rate is governed by the hydrolysis rate. Reaction (11) is known to be facilitated under acidic conditions (pH $<$ 4 i.e., at pH higher than those required to facilitate the hydrolysis) which may occur in our experiments for several reasons. It must be first underlined that in the droplet train technique, the reactions are

taking place over short time scales (less than about 20 ms). Under such conditions, the in-coming gas cannot diffuse deeply into the droplet and the reactions are confined in a very narrow shell close to the droplet surface, at the μm level as defined by the diffuse-reactive length. This has strong impacts on the evolution of the pH at the "interface" which will be the driving force for the production of Cl2. This also introduces some restrictions in our ability to study these reactions at various pH due to the current limitations of our detection scheme. Under these conditions, the pH at the surface will be affected by HNO3 which is a product of the hydrolysis of ClONO2. In addition, even at low gas reactant concentration, the impurities present in our gas flows will affect the surface pH, as traces of HNO3 in ClONO2 are unavoidable. To minimize the influence of the impurities (less than a few % of the ClONO2 concentration), our experiments were conducted under acidic conditions (pH č 4). These observations do not allow us to convert the Cl2 production into a quantitative information as it is due to a complex reaction mechanism. Therefore this Cl2 production exhibits a highly non-linear behaviour on the experimental conditions and cannot be transposed directly into other conditions. However, this expected Cl2 generation is not a direct outcome of this study. More interestingly is the evidence that this production is due to a complex reaction mechanism rather than a direct reaction of Cl- with ClONO2."

Page 1320, Line 26 How much HOCl are "traces" of HOCl present in the ClONO2 source ? Can you at least make en estimate based on the relative strengths of mass spectrometer signals?

The text was modified: "We observed indeed Cl2 as a unique product. Similar observations have already been made by Timonen et al. (1994) or Aguzzi and Rossi (1999) on solid NaCl. However, we have to underline that traces of HOCl in the ClONO2 source may significantly contribute to Cl2 formation (reaction 11). We did not observe any HOCl in our ClONO2 source. However if HOCl was present, even at concentrations below our detection limit, its presence may drastically change the quantitative conclusion about the Cl2 yield. Such an observation prevents us from giving any quantitative

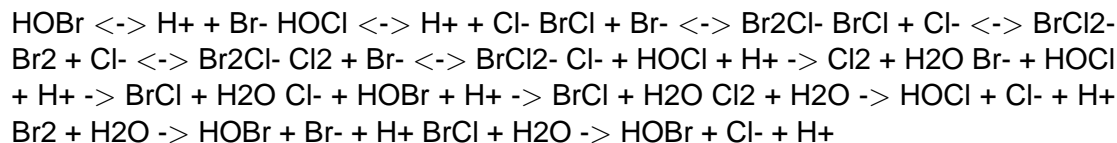assessment on the amount of Cl2 formed by reaction 10."

Page 1322, Line 4 A glance at the data in Figure 3 shows that the error limits on alpha are underestimated. Based on the data in Table 1, I got errors of close to 10 % in the intercept (without weighting), and slightly smaller with weighting. In addition, the data point at 1 M NaBr (Figure 3) is missing from the Table. The authors state that the errors presented are statistical only, and do not include systematic errors. As they quote exactly the same number and error in the abstract, they clearly do not believe that they have any systematic errors, or do not care to think about them. This is sloppy, and especially regrettable when comparisons are made with other datasets. On line 17 they state that a value of 0.23 is consistent with their value of 0.1. How can this be consistent when neither value appear to have any associated errors ? Is the value obtained for alpha consistent with expectations of the uptake coefficient to an aqueous surface. What is the corresponding value for H2SO4 ?

The missing point at 1 M NaBr has been added in Table 1. The evaluation of errors has been also revised (this appears in the abstract and in the text, p 12 and 15 of the present version). They correspond now to 2s + 20% (systematic errors).

Page 1323, Line 1-6 "The above set of reactions fully explains the observed trends in reaction products" This is a purely qualitative statement, showing that the authors have found some reactions that are known to generate the same products as they observe. The "fully explains" is rather optimistic. These equations certainly do not quantitatively explain why Cl2 is the dominant product as it appears to be from Figure 4. This would imply that the rate of release of BrCl from the droplet is much smaller that its rate of reaction with Br-. This will be dependent on the concentration of Br-, which was varied. Do the authors see a dependence on the yield of BrCl and thus also Cl2 on the concentration of Br- ? I do not see why the fact that Aguzzi and Rossi observe BrCl from the reaction of ClONO2 with KBr provides any confirmation of the present results (line 10).

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In this study we measured for the first time, the uptake rate of both ClONO2 and BrONO2 on aqueous droplets containing either chloride or bromide anions. Simultaneously to the observation of the loss of these compounds from the gas phase, we observed the appearance of some products i.e., Cl2, Br2 and BrCl (as expected). However, we can not report any quantitative yields for these products for several reasons which are all linked to the complexity of the chemistry associated with these halogenated species. In fact, in a gas phase containing all these compounds (either as impurities or reaction products), the following (but still incomplete) reaction mechanism is occurring:

HOBr <-> H+ + Br- HOCl <-> H+ + Cl- BrCl + Br- <-> Br2Cl- BrCl + Cl- <-> BrCl2- Br2 + Cl- <-> Br2Cl- Cl2 + Br- <-> BrCl2- Cl- + HOCl + H+ -> Cl2 + H2O Br- + HOCl + H+ -> BrCl + H2O Cl- + HOBr + H+ -> BrCl + H2O Cl2 + H2O -> HOCl + Cl- + H+ Br2 + H2O -> HOBr + Br- + H+ BrCl + H2O -> HOBr + Cl- + H+

This sequence of reactions (along with the others reactions listed in the text) highlights the very strong interplay between all halogenated species in the aqueous phase and the crucial role played by H+ ions. Characterising individual steps and therefore providing meaningful product yields, that can be transposed into real conditions, is far beyond the capabilities of the droplet train technique. On the same basis, working with mixed chloride Ű bromide solutions is probably useless since the product yields would have highly non linear response to the experimental conditions. However, despite the fact that our study cannot provide more insights into the chemistry occurring in the aqueous phase, subsequently to the uptake of ClONO2 and BrONO2, the droplet train technique provides a reliable approach for studying the gas phase loss rates and the associated uptake rates. Our results show that as long as the hydrolysis of ClONO2 and BrONO2 is not suppressed, only bromide can react directly with these compounds due to its higher nucleophilicity compared to chloride.

The Figures 4 and 6 have y-axes that are scaled with "arbitrary units". Does this imply that the authors have made no attempt to calibrate the sensitivity of their detectors.

Surely this has to be done for species such as Cl2 and BrCl and Br2.

As explained in the experimental section, the detectors have been used in an uncalibrated mode since only the relative decay of the gas phase reactants has to be known in order to derive uptake coefficients.

Page 1323, Line 20 "HOBr might be more soluble than HOCl". Might it also be less soluble ? What is the purpose of this statement ?

This sentence was removed.

Page 1324, Line 15 The reaction between BrONO2 and NaCl is said to proceed via initial HOBr formation, followed by the reaction between HOBr and NaCl to form BrCl, which is however acid catalyzed (see comment for ClONO2). It has been shown that the BrCl product is only formed at low pH. The same arguments apply as for HOCl. Why does this reaction proceed in the present experiments ?. It would have been useful to conduct experiments at different pH to test for changes in the yields of e.g. BrCl. Can the authors really rule out that there is a direct (but not rate limiting) reaction between BrONO2 and NaBr ? This may have important repercussions (see Sander, Geophys. Res. Lett. 26, 2857 (1999).

In our experimental conditions (at pH < 4), we effectively suggest again a two-step reaction i.e., first the hydrolysis of BrONO, producing HOBr (reaction 18) which subsequently reacts with NaCl according to: HOBr + NaCl -> BrCl + NaOH (20)

Page 1325, Line 9 The accommodation coefficient of BrONO2 on these aqueous surfaces appears to be lower than the uptake coefficient on aqueous sulfuric acid surfaces (values as high as 0.8 have been measured) and also with uptake to "dry" NaCl or NaBr (Line 20). This would appear to be counter-intuitive. Could the authors speculate some more about this. The sentence "...this could be linked to the nature of their solid surfaces and of its water content....." is inadequate.

The difference in uptake rate between ClONO2 and BrONO2 is puzzling. Neverthe-

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less, we try to discuss more thoroughly this observation by comparing the behaviour of the XONO2 components to other previous observations: "As already performed for ClONO2, we can compare our values with those reported on solid NaCl or NaBr. Aguzzi and Rossi (1999) reported initial uptake coefficients larger than 0.3 and therefore inconsistent with our estimated mass accommodation coefficient. This discrepancy remains unresolved at this time. The uptake coefficient of BrONO2 on sulphuric acid surfaces has also been measured to be relatively large, reaching values of 0.5-0.8 (Hanson et al., 1996). It may therefore be counter intuitive to have an order of magnitude lower values for its uptake on water. To explain this observed trend we can only speculate as there is no other data for the uptake of BrONO2 on water. We can first compare to previous studies on nitryl type compounds. It was shown that the uptake coefficient of ClNO2 on water was larger than that of BrNO2. As already mentioned we also observed that the mass accommodation coefficient of HBr was smaller than that of HCl (Schweitzer et al., 2000). The data on BrONO2 is therefore following these trends which might be related to the Br atom. Although it is difficult to present any quantitative attempt to explain these observations, we can speculate that they are linked to the ability of Br atoms to interact with water molecules at the interface. It is known that bromide ions (and even more strongly iodide anions) present concentration enhancement at the air/water interface, reflecting their capacity to have non-complete solvation shells at the interface. If we extend these observations to the brominated compounds considered here, we can speculate that only a fraction of the in-coming gas will be fully solvated and therefore counted in the calculation of the mass accommodation coefficient which is the probability for a complete phase transfer. If such a surface storage capacity exist, a lowering of the overall measured uptake rate may result."

P1328, Line 3,4 The reference to the work of Sander appears to be incomplete.

The reference has been completed.

P1328, Line 3,4 The reference to the work of Timonen et al. contains chemical formula which require attention.

The reference has been corrected.

P1328, Line 3,4 The first author is Wingenter not Wingetener.

The name of the first author has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1311, 2004.

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